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# 3-Amino alkylated indoles as corrosion inhibitors for mild steel in 1M HCl: Experimental and theoretical studies

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ABSTRACT

The present study describes the influence of ring and ring size of three 3-amino alkylated indoles (AAIs) namely, N-((1H-indol-3-yl)(phenyl)methyl)-N-ethylethanamine (AAI-1), 3-(phenyl(pyrrolidin-1-yl)methyl)-1H-indole (AAI-2) and 3-(phenyl(piperidin-1-yl)methyl)-1H-indole (AAI-3) on mild steel corrosion in 1M HCl solution using gravimetric, electrochemical, surface morphology (SEM, AFM), quantum chemical calculations and molecular dynamics simulations methods. Both experimental and theoretical results showed that the 3-amino alkylated indoles with cyclic amino groups exhibit higher inhibition efficiency compared to the one with opened-chain amino group. The results further suggested that the inhibition efficiency increases with increasing ring size of the amino group such that the piperidine-containing (6-membered ring) 3-amino alkylated indole showed higher inhibition performance than the pyrrolidine-containing (five membered) 3-amino alkylated indole. Experimental results revealed that the inhibition efficiency increases with increasing concentration of the inhibitors. Maximum inhibition efficiencies of 94.34% for AAI-1, 96.08% for AAI-2 and 96.95% for AAI-3 were obtained at 0.862 mM concentration. EIS measurements showed that the studied compounds inhibit mild steel corrosion by adsorbing on the steel surface. Polarization studies revealed that the compounds are cathodic type inhibitors. The adsorption of the studied compounds obeyed the Langmuir adsorption isotherm. SEM and AFM surface morphology analyses also provided evidence of formation of adsorbed film of the AAIs on the steel surface. Theoretical parameters such as $E_{HOMO}$ and electronegativity derived from quantum chemical calculations as well as binding energy derived from molecular dynamics simulations studies adequately corroborate the trend of experimental inhibition efficiencies of the studied inhibitors.



## 1. Introduction

Acid solutions are commonly used for pickling and also for the removal of rust and scales in petroleum industries [1–4]. The use of acid solutions for these industrial activities results in loss corrosion and eventually loss of metals. Addition of organic corrosion inhibitors, which are compounds that contain heteroatoms (e.g. N, O and S), double and triple bonds and aromatic rings has been identified as one of the most practical and economical ways of controlling metal corrosion [5–8]. These compounds inhibit metallic corrosion by becoming adsorbate at metal/electrolyte interfaces in which polar functional groups such $-NH_2$, –OH, —CN, $-NO_2$ etc. and pi-electrons of the double and triple bonds and aromatic rings act as adsorption centers [9–11]. Adsorption of these compounds depends upon several factors including molecular weight, nature of substituents, solution temperature, nature of inhibitor and electrolytes etc. [12,13]. However, most of the previously existing corrosion inhibitors are toxic and non-environmental friendly [14,15]. The current strict measures on environmental regulations and increasing ecological awareness have shifted the attentions of corrosion control experts toward the development of efficient and environmentally benign corrosion inhibitors [16–18]. In this direction, multicomponent reactions (MCRs), which combine three or more substrates is one of the most relevant current approaches that are able to produce several bonds in one step [19–22]. In addition, the MCRs have other several advantages including operational simplicity, facile automation and minimized waste generation, because of the reduction in the number of work-up, extraction and purification stages [19,23]. In spite of the theory of famous ancient philosopher of Greece, namely Aristotle, the "No Coopora nisi Fluida" which means "No reaction takes place in absence of solvent", in recent years organic synthesis in solid

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phase (solvent free condition) attracted great deal of attraction due to their reduce pollution, low costs, and simplicity in process and handling [24]. Certainly, in several cases, solvent free reactions takes place with high yield and selectivity than does their solution counterpart because of the more tight and regular arrangement of molecules in the crystal form [20,25]. Furthermore, "green chemistry" emphasizes the optimization of synthetic methodologies to reduce environmental pollution, cost and tedious work-ups. This new challenge has led to a growing interest in the field of organic synthesis using catalyst derived from natural resources [26,27]. In asymmetric organocatalysis, consumption of L-proline provides the means of upholding the essential principles of green chemistry as it is directly isolated from natural biological sources without use of any hazardous chemical and/or solvents such as DMSO, DMF and other chlorinated solvents [28]. Literature survey reveals that indole and its derivatives act as efficient metallic corrosion in different electrolytic media [29–33]. These compounds inhibit metallic corrosion by becoming adsorbate at the metal/electrolyte interface in which indole moiety acts as adsorption center.

In the present study, the effect of the type of amine (opened chain or cyclic) as well as ring size of cyclic amine on the corrosion inhibition efficiency of three newly synthesized 3-amino alkylated indoles (AAIs) namely, N-((1H-indol-3-yl)(phenyl)methyl)-N-ethylethanamine (AAI-1), 3-(phenyl(pyrrolidin-1-yl)methyl)-1H-indole (AAI-2) and 3-(phenyl(piperidin-1-yl)methyl)-1H-indole (AAI-3) on mild steel corrosion in 1M HCl solution is being investigated for the first time. The corrosion inhibition performances of the three newly synthesized AAIs were determined using weight loss, electrochemical impedance spectroscopy (EIS), potentiodynamic polarization, scanning electron microscopy (SEM), and atomic force microscopy (AFM) techniques. Quantum chemical calculations and molecular dynamics simulations studies were also carried out to provide more insights into the theoretical explanations of the inhibition activities of the studied compounds.

## 2. Experimental section

### 2.1. Materials

#### 2.1.1. Electrode and reagents

The mild steel specimens for weight loss, electrochemical and surface measurements were cut form commercially available mild steel sheet having chemical composition (wt%): C (0.076), Mn (0.192), P (0.012), Si (0.026), Cr (0.050), Al (0.023), and Fe (balance). The exposed surface of the working electrodes were cleaned successively with emery papers of different grade (600, 800, 1000, and 1200), washed with deionized water, degreased with acetone, ultrasonically cleaned with ethanol and stored in moisture free desiccator before used in the experiments. Hydrochloric acid (HCl, 37%, MERCK) and double distilled water were used for preparation of test solution (1M HCl).

#### 2.1.2. Inhibitors synthesis

3-amino alkylated indoles (AAIs) used in the present study were synthesized by the method described earlier [34]. In a typical experimental procedure, 1 mmol of the aldehyde, 1 mmol of the secondary amine, 1 mmol indole and 30 mol% of the L proline were placed in a round-bottom flask and stirred at room temperature. The progress and completion of the reaction was monitor by TLC method. After, completion of the reaction, the reaction mixtures were diluted with water and then extracted with ethyl acetate. The crude products were purified by column chromatography to give the corresponding inhibitors. Synthetic scheme of investigated inhibitors is given in Fig. 1 and chemical structures, abbreviations, IUPAC name and analytical data of the synthesized compounds are given in Table 1.

### 2.2. Methods

#### 2.2.1. Weight loss measurements

Cleaned, dried and accurately weighted mild steel specimens having dimension 2.5 cm × 2.0 cm × 0.025 cm were immersed in 1M HCl without and with different concentrations of AAIs for 3 h. After elapsed time, these specimens were removed, washed with distilled water and acetone, dried in moisture free desiccator, and again weighed accurately. To ensure the reproducibility of the weight loss results, each experiment was triply performed and mean values are reported at each concentration. From the calculated weight loss, inhibition efficiency ($\eta\%$) was derived using following relationship [35]:

$$\eta\% = \frac{w_0 - w_i}{w_0} \times 100 \quad (1)$$

where $w_0$ and $w_i$ are the weight loss values in the absence and presence of AAIs at different concentrations, respectively.

#### 2.2.2. Electrochemical measurements

The mild steel specimens with exposed area 1 $cm^2$ (one sided) were utilized for all electrochemical measurements were performed under potentiodynamic condition using Gamry Potentiostat/Galvanostat (Model G-300) instrument. Gamry Echem Analyst 5.0 software installed in the computer was used to fit and analyzed all electrochemical data. The instrument consist of a mild steel working electrode (WE), platinum as a counter electrode and a saturated calomel electrode (SCE) as a reference electrode. Before starting the electrochemical experiments, the working electrode were allowed to corrode freely for 30 min in order to attain steady open circuit potential (OCP). During polarization measurements, the cathodic and anodic Tafel slopes were recorded by changing the electrode potential from 0.25 to + 0.25 V vs corrosion potential ($E_{corr}$) at a constant sweep rate of 1.0 mV $s^{-1}$. The corrosion current density ($i_{corr}$) was calculated by extrapolating the linear segments

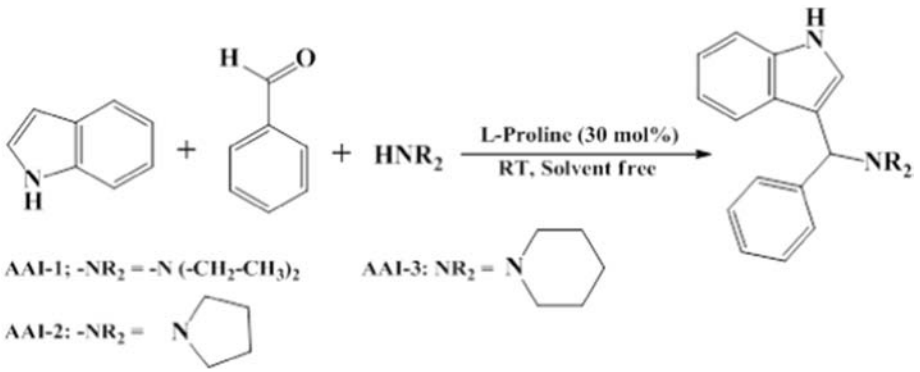


**Fig. 1.** Synthetic route of studied AAIs.